18. On Flexibility of the Cellulose Molecules in Dilute Solution

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Two models of a rod-like macromolecule regularly crooked zigzag on the same plane were adopted. These models may represent a medium state between the rigid rod molecule and the flexible molecule of pearlnecklace type assumed by Debye-Bueche. Based on these models, the following two equations are obtained for the viscosity of macromolecules in dilute solution.

$$\eta_{sp}/c = \sin^2\theta \; l^3/50625\, m \qquad (1)$$

$$\eta_{sp}/c = \{k\pi\ (1+\cot\theta)\}^{-2} l^3/3164\, m \qquad (2)$$

where

η_{sp}: specific viscosity, c: concentration g./1000 c.c.,

2θ: angle between two elements (segments),

l: total length of a macromolecule,

m: molecular weight,

Available intrinsic viscosity and molecular weight data for cellulose derivatives have been employed to calculate flex angle and the distance between ends of chain molecules. An example for nitrocellulose is shown in Table 1.

It is seen from the table that nitrocellulose of low molecular weight is scarcely crooked, but with increasing molecular weight the flex angle becomes sharper.

Table 1. Flexibility of nitrocellulose molecule in acetone.

Molecular weight (osmotic.)	D. P. (osmotic.)	η_{sp}/c (obs.)	l (Å) (calc.)	Flex angle $2\theta(2)$	$2\theta(1)$	Distance between ends (Å)
17000	61	0.047	305	(180)	(180)	(305)
41000	145	0.116	725	104	118	570
45000	163	0.143	815	100	112	626
81000	291	0.224	1455	65	74	775
129000	465	0.387	2325	53	59	1025
146000	524	0.438	2620	50	55	1100
186000	670	0.560	3350	44	48	1240
195000	698	0.591	3490	43	45	1256
286000	1020	0.850	5100	35	36	1530
396000	1420	1.154	7100	29	31	1777